Laser-Induced,Blackbody-Radiation-Assisted Rovibrational Cooling of Linear Triatomic Molecules

B Taraphdar[1†], A Sinha[1] and N Deb[1†]

[1]School of Chemical Sciences, Indian Association for the Cultivation of Science, Kolkata 700032, India

Synopsis The preparation of state-specific molecular ions is essential for precision measurements and studies of cold ion–molecule collisions. However, ambient blackbody radiation (BBR) can drive rotational-state populations toward a Boltzmann distribution, reducing state purity within a few tens of seconds. This work investigates BBR-induced rovibrational dynamics, estimates state lifetimes, and explores cooling schemes to preserve well-defined quantum states for state-selective ion–molecule collision studies. While such dynamics and cooling schemes have been studied for diatomic, [1] symmetric-top (NH_3^+), [2] and acetylene ($C_2H_2^+$) ions, [3] linear triatomic molecular ions remain largely unexplored. This work therefore aims to extend these studies and develop strategies for maintaining rotational-state purity in such systems.

For precision measurements, ion-trap experiments, and cold ion–molecule collision studies, the preparation of molecular ions in well-defined quantum states is essential. Recent experimental studies have demonstrated that the internal quantum states of reactants can significantly influence reaction outcomes. Combining Coulomb-crystallized ions with Stark-deflected or cryogenically cooled neutral beams offers the possibility of investigating reactions involving molecules prepared in their absolute ground states. [5] Furthermore, recent advances in merged-beam experiments have opened new avenues for studying rotational-state-selective reactions. However, state-selective preparation alone is insufficient; the ions must also retain their quantum-state purity over the experimental timescale. Consequently, theoretical investigations of laser-induced cooling schemes are crucial for both the preparation and preservation of molecular ions in well-defined quantum states.

Although laser-induced control of molecular internal states has been extensively investigated for diatomic molecules, [1] symmetric-top molecules (NH_3^+), [2] as well as for acetylene ($C_2H_2^+$), [3] its application to other polyatomic systems, particularly linear triatomic molecules, remains relatively unexplored. In this work, we investigate laser-induced, blackbody-radiation-assisted (BBR-assisted) rovibrational cooling of linear triatomic molecular ions, focusing on CO_2^+ because of its relevance to astrochemistry. The CO_2^+ ion exhibits significant Renner–Teller and spin–orbit interactions and has a rotational constant of approximately $0.38\ \mathrm{cm}^{-1}$. Its ground electronic state is an inverted $^2\Pi$ state, with the rotational and electronic angular momenta exhibiting intermediate Hund's case. [4] The molecular energy levels are determined by solving the appropriate rotational Hamiltonian, accounting for the relevant interactions. The resulting energy-level structure is then used to simulate BBR-induced population dynamics by incorporating the relevant spectroscopic selection rules and transition rates into a rate-equation model. Building on this framework, we investigate laser-induced cooling schemes that exploit BBR-mediated transitions to redistribute molecular populations towards selected low-lying quantum states.

References

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†E-mail: taraphdar.brotin03@gmail.com
†E-mail: nabanita.deb@iacs.res.in